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Direct Methods for Incommensurate Intergrowth Compounds. III. Solving the Average Structure in Multidimensional Space

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Abstract

A multidimensional direct method is proposed for *ab initio* phasing of the main reflections of incommensurate intergrowth compounds. This method represents an objective procedure for solving the average structure of composite crystals in multidimensional space. The 'normalized structure factors' are calculated separately for different subsets of main reflections. The derivation of phase information of the reflections and the refinement are performed in multidimensional space. The proposed procedure is tested with known structures of the inorganic misfit layer compounds (LaS)_{1.14}NbS₂ and (PbS)_{1.18}TiS₂. The results show that the phases of the reflections thus obtained are sufficiently accurate to reveal the average structures of these composite crystals.

1. Introduction

According to their basic structures, two classes of incommensurate structures can be distinguished (de Wolff, 1974; Janner & Janssen, 1980*b*). The first has a three-dimensional periodic basic structure while the other has a composite basic structure that consists of two or more interpenetrating mutually incommensurate three-dimensional crystal structures. The latter is the so-called composite structure or incommensurate intergrowth compound, the basic structure of which possesses periodicity only in four- or higher-dimensional space. The *d*-dimensional incommensurate structures are well described in the context of the (3 + *d*)-dimensional superspace (de Wolff, 1974; Janner & Janssen, 1980*a,b*; de Wolff, Janssen & Janner, 1981; Janner, Janssen & de Wolff, 1983; Yamamoto, 1982; van Smaalen, 1992).

Multidimensional direct methods have been proposed and successfully used for solving a number of one-dimensional incommensurately modulated structures with three-dimensional basic structures (Hao, Liu & Fan, 1987; Xiang, Fan, Wu, Li & Pan, 1990; Mo *et al.*, 1992; Fu *et al.*, 1994, 1995; Lam *et al.*,

1995). The procedure has been programmed in *DIMS* by Fu & Fan (1994). In papers I and II of this series (Fan, van Smaalen, Lam & Beurskens, 1993; Sha, Fan, van Smaalen, Lam & Beurskens, 1994), this method has been extended to composite structures for deriving phases of the satellite reflections, and thus to determine the modulation, once the basic structure is known.

The basic structure of incommensurate composite crystals is determined by three classes of reflections: reflections mainly due to the first subsystem, reflections mainly due to the second subsystem and reflections common to both subsystems. In addition, the modulation gives rise to satellite reflections. The structure factors of the common reflections are the sums of the structure factors arising from the individual subsystems. Therefore, the intensities of these reflections cannot be separated into contributions from single subsystems. Consequently, they are not available for a separate treatment of the subsystems in crystallographic methods, such as direct methods or Fourier methods.

The common reflections comprise one reciprocal-lattice plane going through the origin and thus contain many strong and important reflections. Since standard direct methods depend on the availability of all strong reflections, they are bound to fail. In any case, omission of many strong reflections will severely hamper the interpretation of Fourier maps, which are required to derive the structure after the phases of the reflections have been determined. Indexing all reflections corresponding to the basic structure of a composite crystal requires at least four indices and, unlike the case of modulated structures, standard crystallography fails for the determination of the basic (or average) structure of incommensurate composite crystals. It appears to be more difficult to solve the average structure of a composite structure than to determine its modulation once the average structure is known. This is due to the fact that the modulation can be determined through the average structure without even measuring the intensities of satellites and that the composite average structure

itself does not have three-dimensional periodicity and a straightforward way is not available to solve its structure.

In this paper, we propose a procedure to derive the phases of main reflections of an incommensurate intergrowth compound using direct methods in multidimensional space. This method provides a straightforward and objective way to solve the average structure of composite crystals. Results of tests are presented with the known structures of the inorganic misfit layer compounds $(\text{LaS})_{1.14}\text{NbS}_2$ and $(\text{PbS})_{1.18}\text{TiS}_2$.

2. The method

Incommensurate intergrowth compounds can be considered as a coherent combination of two or more modulated structures (Janner & Janssen, 1980*b*; van Smaalen, 1992). Each of the structures (subsystems) is characterized by a unit cell and a set of modulation wave vectors. The diffraction pattern has main reflections at the nodes of the reciprocal lattice of each subsystem and has satellites at positions defined by the modulation wave vectors. For convenience, we consider in the following only the incommensurate intergrowth compounds with two subsystems having a common plane in their reciprocal lattices, thus providing only a single incommensurate direction. The reflection data are indexed with four integer indices $\mathbf{H} = (hklm)$, which refer to a set of four reciprocal-lattice vectors $\mathbf{M}^* = \{\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*, \mathbf{a}_4^*\}$. In the present setting, the two subsystems have \mathbf{a}_2^* and \mathbf{a}_3^* in common. Thus, the basic structure of the first subsystem is associated with the main reflections $hkl0$, while that of the second subsystem is associated with the main reflections $Oklm$. The reflections $hklm$ ($h \neq 0, m \neq 0$) are satellite reflections. The special main reflections $Ok00$ are common to both subsystems.

According to the multidimensional Sayre equation (Hao, Liu & Fan, 1987) for an incommensurately modulated structure, we have the following phase relation:

$$\begin{aligned} \varphi[F(\mathbf{H})] = \varphi \left[\sum_{\mathbf{H}'} F_{\text{main}}(\mathbf{H}') F_{\text{main}}(\mathbf{H} - \mathbf{H}') \right. \\ \left. + \sum_{\mathbf{H}'} F_{\text{main}}(\mathbf{H}') F_{\text{sat}}(\mathbf{H} - \mathbf{H}') \right. \\ \left. + \sum_{\mathbf{H}'} F_{\text{sat}}(\mathbf{H}') F_{\text{sat}}(\mathbf{H} - \mathbf{H}') \right], \quad (1) \end{aligned}$$

where $\varphi[F(\mathbf{H})]$ denotes the phase of $F(\mathbf{H})$ and $F(\mathbf{H})$ is the structure factor of the reflection with indices \mathbf{H} . The subscript main stands for main reflections while sat stands for satellites. As the intensities of satellites are on average much weaker than those of main reflections, the last two summations on the right-hand side of (1) are

negligible in comparison with the first. We thus have, to a first approximation:

$$\varphi[F_{\text{main}}(\mathbf{H})] = \varphi \left[\sum_{\mathbf{H}'} F_{\text{main}}(\mathbf{H}') F_{\text{main}}(\mathbf{H} - \mathbf{H}') \right]. \quad (2)$$

This implies that it is possible to solve the basic structure in multidimensional space using only main reflections. For incommensurately modulated structures having a three-dimensional basic structure, the phases of main reflections can be derived by conventional direct methods (Hao, Liu & Fan, 1987; Fu *et al.*, 1995). For incommensurate intergrowth compounds, however, the phases of main reflections have to be derived by a multidimensional direct-methods procedure because the basic structure is a four- or higher-dimensional periodic structure. Details of the procedure are given below.

First, the main reflections are divided into three subsets: (i) reflections due to subsystem 1, in the present example, these are reflections $hkl0$ with $h \neq 0$; (ii) reflections due to subsystem 2, which are reflections $Oklm$ with $m \neq 0$; and (iii) reflections with contributions from both subsystems, which are the reflections $Ok00$. Reflections in (i) are associated with the basic structure of the first subsystem, those in (ii) are associated with the basic structure of the second subsystem while reflections $Ok00$ have contributions from the atoms in both subsystems. Secondly, the structure factors in (i) and (ii) are normalized separately in a way similar to that with conventional three-dimensional direct methods using the following formula:

$$E(\mathbf{H}) = F(\mathbf{H}) V_\nu / \left(K^2 \sum_{j=1}^{N_\nu} f_{\nu j}^2 \right)^{1/2}, \quad (3)$$

where $\nu = 1$ or 2 for the first or the second subsystem, respectively. N_ν stands for the number of atoms in the unit cell of the basic structure of the ν th subsystem while $f_{\nu j}$ stands for the atomic scattering factors; V_ν is the volume of the unit cell of subsystem ν , taking into account the possibility that different subsystems may have different centerings; K is the scale factor. The structure factors in (iii) are normalized in a similar way, but taking into account that all atoms contribute to these reflections. That is,

$$E(\mathbf{H}) = F(\mathbf{H}) \left(\sum_{j=1}^{N_1} f_{1j}^2 / V_1^2 + \sum_{j=1}^{N_2} f_{2j}^2 / V_2^2 \right)^{-1/2} / K. \quad (4)$$

With these 'normalized structure factors', a direct-method program using a random starting tangent refinement procedure (Yao, 1981) was written in four-dimensional space. The combined figure of merit, CFOM, is used in the program for picking out the correct solution.

$$\begin{aligned} \text{CFOM} = & W_1(A - A_{\min})/(A_{\max} - A_{\min}) \\ & + W_2[(\psi_0)_{\max} - \psi_0]/[(\psi_0)_{\max} - (\psi_0)_{\min}] \\ & + W_3(R_{\max} - R)/(R_{\max} - R_{\min}), \end{aligned} \quad (5)$$

where A , ψ_0 and R are, respectively, the absolute, the psi-zero and the residual figure of merit as defined in *MULTAN* (Main *et al.*, 1980).

3. Tests and results

3.1. $(\text{LaS})_{1.14}\text{NbS}_2$

The modulated structure of $(\text{LaS})_{1.14}\text{NbS}_2$ was determined by van Smaalen (1991) using X-ray diffraction data of Meerschaut, Rabu & Rouxel (1989) and employing the superspace formalism. The compound consists of two subsystems: NbS_2 and LaS . The first subsystem (NbS_2) has superspace group $Fm2m(\alpha, 0, 0)\bar{1}1s$ with lattice parameters $a_{11} = 3.310$, $a_{12} = 5.793$ and $a_{13} = 23.043$ Å. The second subsystem has superspace group $Cm2m(\alpha^{-1}, 0, 0)\bar{1}11$ with lattice parameters $a_{21} = 5.828$, $a_{22} = 5.793$ and $a_{23} = 23.043$ Å. Here, $\alpha = a_{11}/a_{12} = 0.568$ represents the mutual incommensurability of the two a axes of the two subsystems. There are 624 main reflections and 276 satellites, which are indexed with four integer indices, $hklm$, based on the set of reciprocal vectors $\{\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*, \mathbf{a}_4^*\}$. These vectors are defined as $\mathbf{a}_1^* = \mathbf{a}_{11}^*$, $\mathbf{a}_2^* = \mathbf{a}_{12}^*$, $\mathbf{a}_3^* = \mathbf{a}_{13}^*$ and $\mathbf{a}_4^* = \mathbf{a}_{21}^*$. The 'normalized structure factors' were calculated using (3) and (4). 312 main reflections with large E values were used for direct-method phasing, which include 147 $hkl0$ reflections from the first subsystem NbS_2 , 192 $Oklm$ reflections from the second subsystem LaS and 27 $OkI0$ common reflections from both subsystems. Among the 1000 random starting trials, set 702 has the highest combined figure of merit with an average phase error of 40° for the 312 main reflections. Average phase errors for different subsets resulting from the direct method are listed in Table 1.

A two-dimensional (2D) section of the 4D Fourier map at the position of the La atom is shown in Fig. 1. It reveals the line-like atomic character of La along the additional dimension (that is x_1 for the LaS subsystem and x_4 for the NbS_2 subsystem). Its appearance is similar to that in the Fourier map calculated with phases from the refinement, and it again shows that main reflections are not sufficient to resolve the modulation (Fan *et al.*, 1993).

All atoms lie in mirror planes, which themselves are parallel to the common periodic plane $(\mathbf{a}_{s2}, \mathbf{a}_{s3})$. Fig. 2(a) shows an (x_2, x_3) section of the 4D Fourier map at the positions of the atoms in the NbS_2 subsystem (characterized by $x_1 = 0$) as well as of the atoms in the LaS subsystems ($x_4 = 0$). The observed maxima correspond to the atomic positions of LaS and of Nb ,

Table 1. *Phasing results for $(\text{LaS})_{1.14}\text{NbS}_2$*

The average phase errors were calculated for all 312 main reflections and for the different subsets of reflections $hkl0$, $Oklm$ and $OkI0$.

Number of reflections	Index type	Average phase error ($^\circ$)
312	$hklm$	40
147	$hkl0$	58
192	$Oklm$	28
27	$OkI0$	54

as can be checked by comparing Fig. 2(a) with the Fourier map obtained using phases from the refinement (Fig. 2b). The S atoms of the NbS_2 subsystem are not completely resolved. Intensity is found at the two possible alternative positions for these atoms. This correlates with the average phase errors obtained for the different subsets. For the reflections of the LaS subsystem, this is 28° and the S atom is clearly resolved. For the reflections of the NbS_2 subsystem, it is 58° . Although Nb can still be found, it apparently is not sufficient to uniquely determine the S atoms. This incompleteness might be due to the fact that there are much fewer reflections available in the data set than there are reflections for the second example described below. On the other hand, it would not be difficult to obtain the complete structure through Fourier recycling based on the direct-method map (Fig. 2a).

3.2. $(\text{PbS})_{1.18}\text{TiS}_2$

$(\text{PbS})_{1.18}\text{TiS}_2$ is similar to $(\text{LaS})_{1.14}\text{NbS}_2$ but with monoclinic symmetry $C2_1/m(\alpha, 0, 0)\bar{1}1$ (van Smaalen, Meetsma, Wiegers & de Boer, 1991). There are 1462 main reflections, among which 731

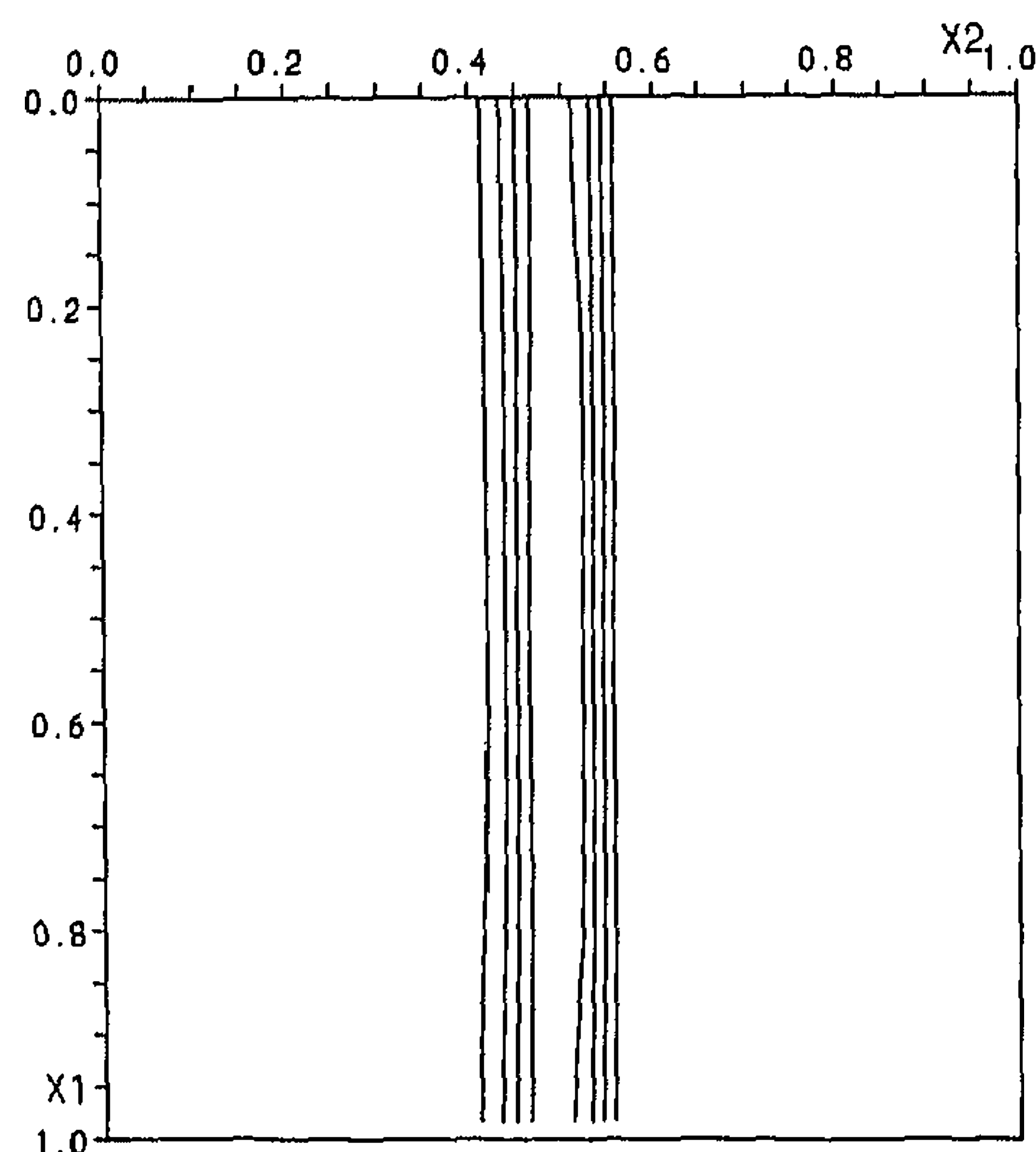


Fig. 1. Two-dimensional section of the four-dimensional Fourier map of $(\text{LaS})_{1.14}\text{NbS}_2$ at the position of the La atom ($x_3 = 0.174$ and $x_4 = 0$), calculated with observed structure-factor amplitudes and phases from the direct-methods procedure. The string-like appearance along the additional dimension (x_1) is obvious and it is similar to the same section of the 4D Fourier calculated with phases from the refinement.

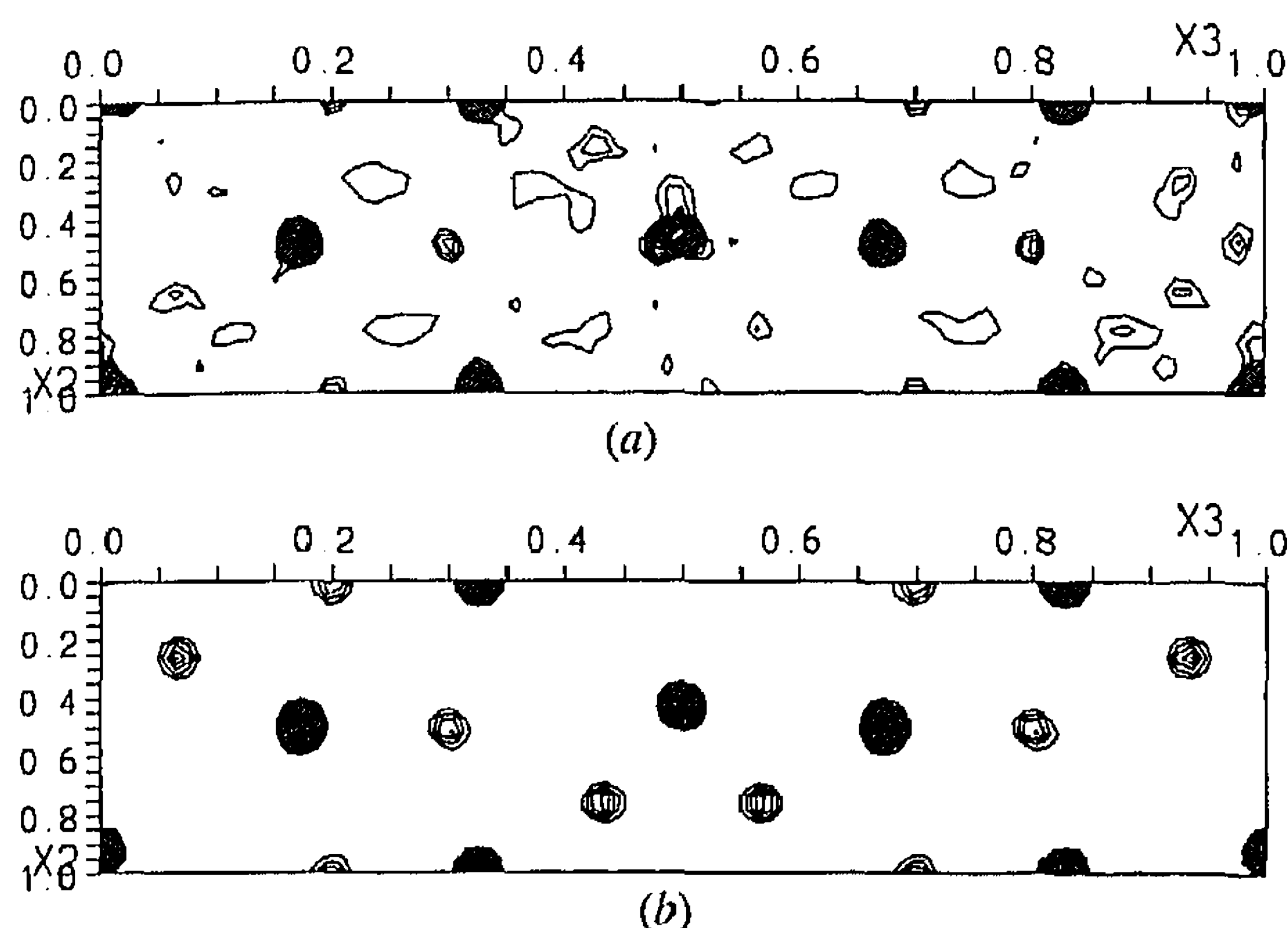


Fig. 2. Two-dimensional section of the 4D Fourier map of $(\text{LaS})_{1.14}\text{NbS}_2$ showing the common periodic plane at $x_1 = 0$ and $x_4 = 0$. (a) Obtained with 312 main reflections and their phases from the direct-methods procedure. (b) Obtained with all 624 main reflections and their phases from the refinement of the basic structure. In each case, with the assumption that the maximum in this plane corresponds to the heavy atom (La at $x_1 = x_2 = 0$), the contour intervals were chosen such that there are five up to the maximum of an S atom.

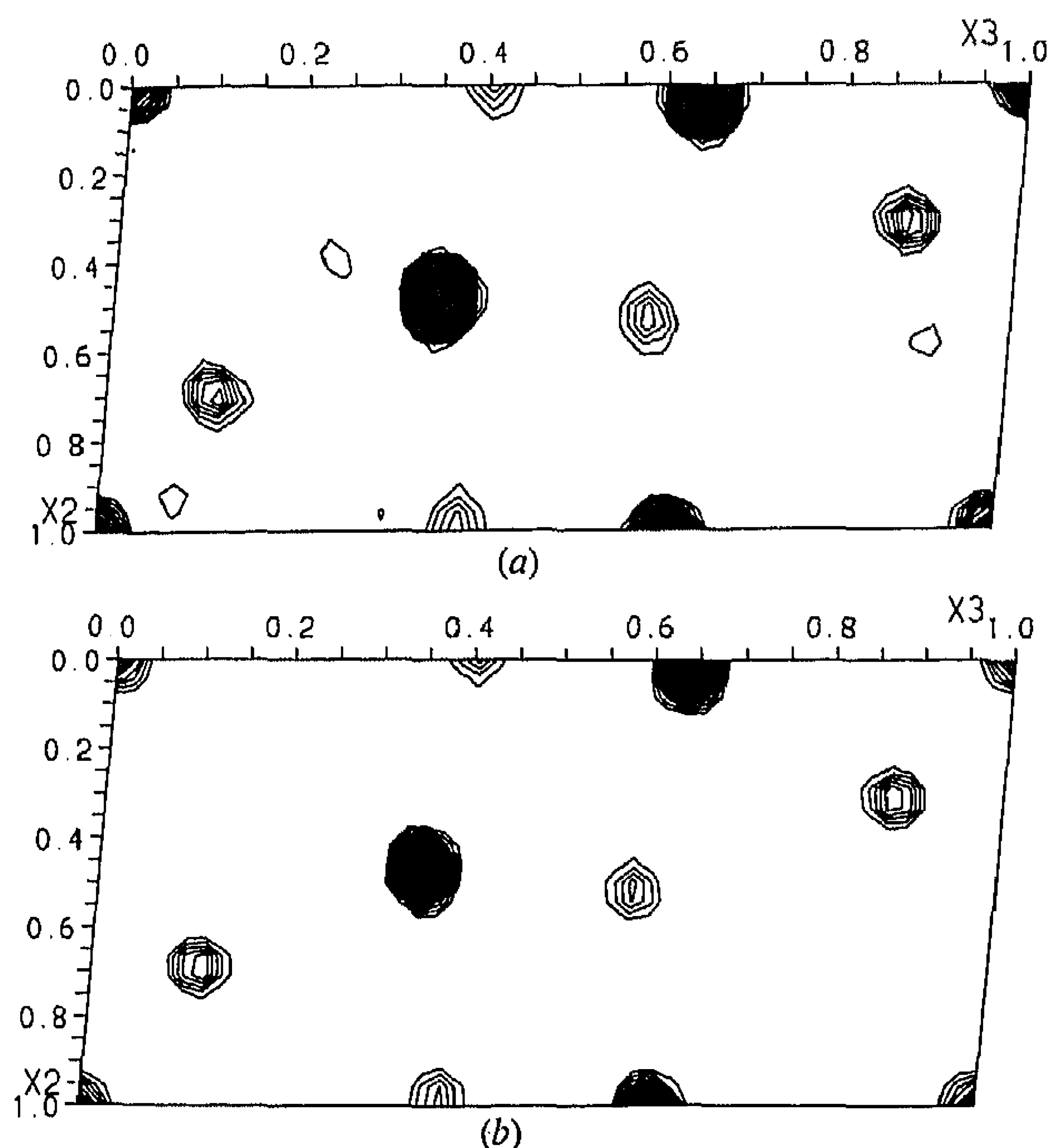


Fig. 3. Two-dimensional section of the 4D Fourier map of $(\text{PbS})_{1.18}\text{TiS}_2$ showing the common periodic plane at $x_1 = 0$ and $x_4 = 0.25$. (a) Obtained with 731 main reflections and their phases from the direct-methods procedure. (b) Obtained with 1462 main reflections and their phases from the refinement of the basic structure. In each case, with the assumption that the maximum in this plane corresponds to the heavy atom (Pb at $x_2 = 0$ and $x_3 = 0.64$), the contour intervals were chosen such that there are five of them between zero and the maximum of an S atom.

Table 2. Phasing results for $(\text{PbS})_{1.18}\text{TiS}_2$

The average phase errors were calculated for all 731 main reflections and for the different subsets of reflections $hkl0$, $Oklm$ and $Ok0$.

Number of reflections	Index type	Average phase error ($^\circ$)
731	$hklm$	20
353	$hkl0$	22
448	$Oklm$	18
70	$Ok0$	18

having large E values were used for the direct-method phase derivation. These 731 main reflections included 353 $hkl0$ reflections of the subsystem TiS_2 , 448 $Oklm$ reflections of the subsystem PbS and 70 $Ok0$ common reflections from both subsystems. Among the 100 random starting trials, set 2 has the highest combined figure of merit with an average error of 20° (Table 2).

The average phase error here is much smaller than that obtained for $(\text{LaS})_{1.14}\text{NbS}_2$. This shows up in the Fourier map such that now all atoms can be identified (Fig. 3a). The noise is much less than in the case of $(\text{LaS})_{1.14}\text{NbS}_2$ and the Fourier map calculated with the phases obtained by direct methods and that calculated with phases from the refinement are more alike than for $(\text{LaS})_{1.14}\text{NbS}_2$ (Fig. 3).

The line-like character of the atoms is illustrated by considering sections of the Fourier map at different

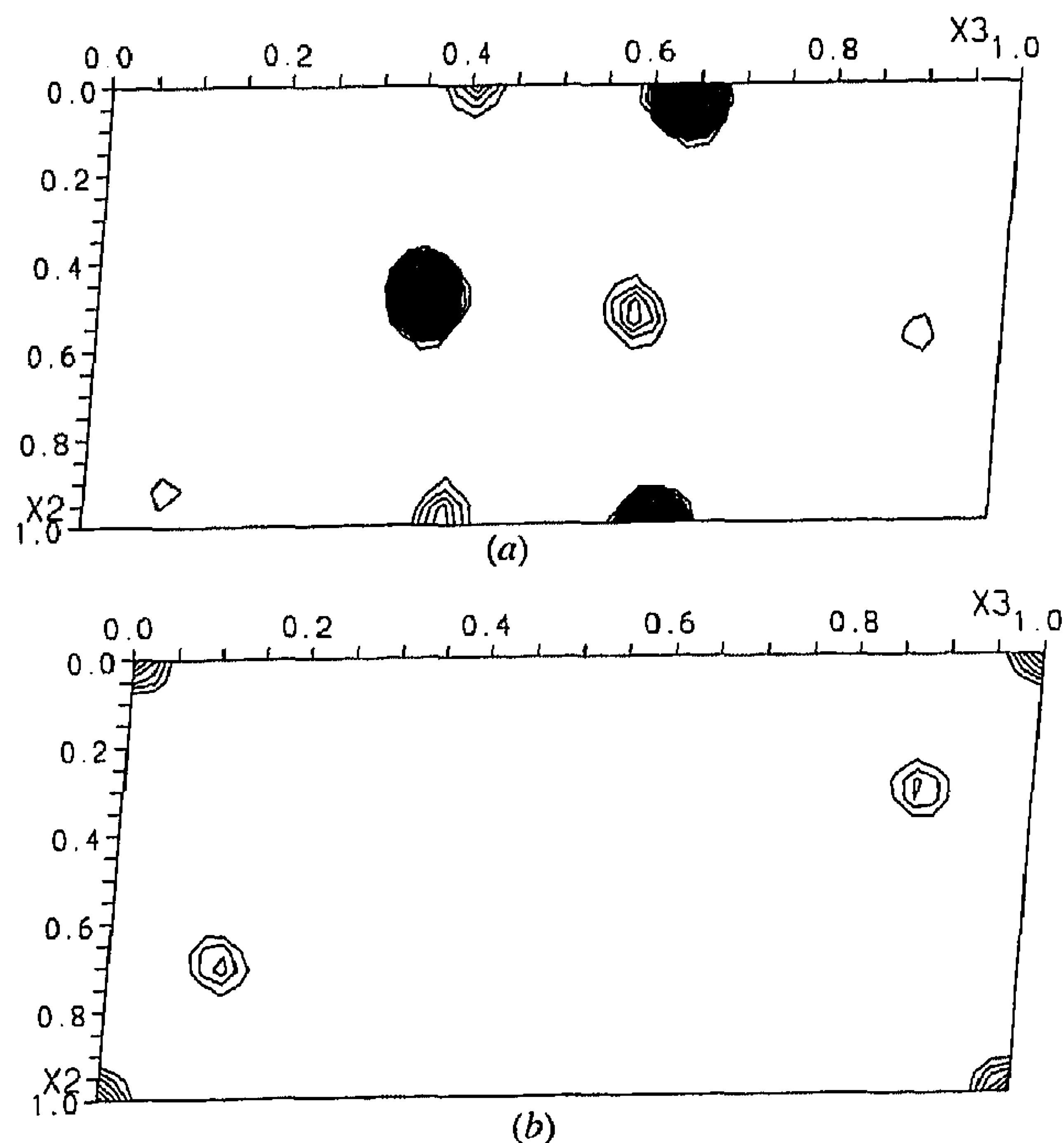


Fig. 4. Two-dimensional section of the 4D Fourier map of $(\text{PbS})_{1.18}\text{TiS}_2$ obtained with phases from the direct-methods procedure and showing a plane parallel to the common periodic plane. (a) At $x_1 = 0.25$ and $x_4 = 0.25$ with atoms of the second subsystem only. (b) At $x_1 = 0$ and $x_4 = 0$ with atoms of the first subsystem only.

values of x_1 and x_4 . For x_1 different from zero, we move out of the mirror plane in the first subsystem and only atoms of the second subsystem (LaS) are found (Fig. 4a). This shows that x_1 is the continuous variable or fourth dimension for the second subsystem. Alternatively, for x_4 different from 0.25, only the atoms of the first subsystems are found (Fig. 4b).

4. Conclusions

A direct-methods procedure has been derived that makes it possible to determine the basic structures of incommensurate composite crystals. This method has been applied to two representatives from the class of inorganic misfit layer compounds. For $(\text{PbS})_{1.18}\text{TiS}_2$, an average phase error of 22° was obtained and all atoms could be located in the Fourier map. For $(\text{LaS})_{1.14}\text{NbS}_2$, an average phase error of 40° was obtained. The Fourier map revealed all heavy atoms and some of the S atoms. In both cases, not only the positions but also the chemical nature of the maxima could be identified correctly.

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